

cavities, where its solid condition would tend to its permanent preservation.

The sedimentary limestones contain frequently crystalline calcite cementing together the grains of amorphous mineral matter. Changes in temperature, causing unequal expansion of this calcite in different directions, by reason of the form of its crystals, might in the course of time modify the process by changing the internal structure of the rock. The presence of salt in solution and the solvent action of carbonic acid would no doubt exert an important influence, although its nature could not be foreseen.

The occurrence of petroleum in the fossil shells of mollusks and in the cells of corals would then have no more geological significance than its occurrence in geodes, or in cavities in rocks, or the presence of solid bitumen in hollow quartz crystals or in sphalerite, as all such cases are perhaps attributable to one and the same source, namely, to its presence formerly in a state of wide distribution in the pores of the rock.

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## ON THE COMPOSITION OF AMERICAN PETROLEUM.

BY CHARLES F. MABERY.

(*Read February 5, 1897.*)

Petroleum is found in Pennsylvania in sandstones of various formations; in southern Ohio in the Berea grit and other sands; in Ohio in the Trenton limestone; in Canada in the Corniferous sandstone; in California, Texas, Colorado, and other American fields in shales and sandstone formations, which represent in general the geological strata in which are the various oil fields in Russia, Roumania, Germany and Austria, Japan, India, etc. Crude oils show great variation in their physical properties, such as color, specific gravity and odor, and differences in their chemical reactions depending on variation in composition.

The first systematic investigation for the purpose of ascertaining the composition of American petroleum was made by Pelouze and Cahours, who referred the entire body of crude oil, including paraffine, to the series homologous with marsh gas,  $C_nH_{2n+2}$ . At about the same time, 1862, C. M. Warren began a study of Pennsylvania

oil, in which he subjected the various refinery distillates to a prolonged course of fractional distillations in a special form of regulated condenser which he devised for such distillations. He separated distillates at  $0^{\circ}$ ,  $8^{\circ}$ - $9^{\circ}$ ,  $30^{\circ}$ ,  $37^{\circ}$ ,  $61^{\circ}$ ,  $68^{\circ}$ ,  $90^{\circ}$ ,  $98^{\circ}$ ,  $119^{\circ}.5$ ,  $127^{\circ}.5$  and at  $150^{\circ}.8$ , of the series  $C_nH_{2n+2}$ , and of the series  $C_nH_{2n}$ , members at  $174^{\circ}.9$ ,  $195^{\circ}.8$ ,  $216^{\circ}.2$ .

In connection with the discovery by synthesis of the hydrocarbons, hexane and heptane, Schorlemmer, in 1865, separated the hydrocarbons  $C_6H_{14}$  and  $C_7H_{18}$ , boiling at  $60^{\circ}$  and  $90^{\circ}$ . After Warren's results were published, he admitted the others at  $38^{\circ}$ ,  $68^{\circ}$  and  $98^{\circ}$ . Schorlemmer also separated an octane at  $125^{\circ}$ . He corrected the work of Pelouze and Cahours with reference to boiling points. At about the same time in 1880, Beilstein and Kurbatiff and Schutzenberger and Jonine undertook an examination of the Caucasus petroleum, and identified hexahydro-aromatic compounds at  $97^{\circ}$  and at  $118^{\circ}$ . The former chemists also found hexahydroisoxylol at  $118^{\circ}$  in American petroleum. Soon afterward Markownikoff separated a long series of the naphthenes at  $69^{\circ}$ ,  $97^{\circ}$ ,  $118^{\circ}.5$ ,  $136^{\circ}$ ,  $162^{\circ}$ ,  $182^{\circ}$ ,  $216^{\circ}$ , and several members with higher boiling points. Markownikoff also found numerous aromatic hydrocarbons of the series  $C_nH_{2n-6}$ , and of other series with less hydrogen.

Various examinations of lesser magnitude have been undertaken, in a more or less superficial manner. Engler showed the presence in small quantities of mesitylene and other aromatic hydrocarbons in Pennsylvania petroleum. Among other bodies present in small amounts are the nitrogen compounds, the oxygen compounds, concerning which there is still some question as to the form in which they exist in the crude oil. Recently Zaloziecky has attempted to show the presence of the terpenes, which I recognized by their odor seven years ago (*Proc. Amer. Acad.*, Vol. xxv, 1890). I began the study of petroleum in 1884, and in 1885, soon after the Trenton limestone oil was discovered, I undertook to separate the sulphur constituents. The sulphur compounds in Canadian petroleum were undertaken in 1891, and are still in progress. In 1893, through aid granted by the C. M. Warren Committee of the American Academy of Arts and Sciences, the scope of my work was extended to include broadly the composition of American petroleum with especial reference to Pennsylvania, Ohio and Canadian crude oils. The great field for research includes the portions of petroleum with boiling points above  $220^{\circ}$ , but there are serious difficulties in the way

of reaching satisfactory results with these bodies. In a paper recently published in the Proceedings of the American Academy an account is given of the composition of Pennsylvania, Ohio, Canadian petroleums below  $220^{\circ}$ . The series  $C_nH_{2n+2}$  represents the main body of Pennsylvania and Ohio oils, and of Canadian oil below  $195^{\circ}$ . Aromatic hydrocarbons of the series  $C_nH_{2n-6}$ , are present in considerable quantities.

Careful study of petroleum from different sources with reference to its occurrence and composition indicates that no precise classification of crude oils can be based on these particular features. Accepting Pennsylvania petroleum as typical in its occurrence as a sandstone oil, in its composition, and in the fact that it is a low sulphur oil, even the numerous varieties from different sections and different strata in the same field present great variations in the proportions of the individual constituents. Such oils as the light amber variety from the Berea grit sandstone (Mabery & Dunn, *Amer. Chem. Journ.*, xviii, 1896) in southern Ohio and Virginia show larger proportions of volatile constituents below  $150^{\circ}$ , and those distilling above  $250^{\circ}$ , but less of the intermediary constituents which are looked on in refining as the more valuable illuminants. In attempting a classification with reference to the proportion of sulphur compounds, it appears that the principal components of the typical Pennsylvania oil form the main body of such oils as those from Ohio Trenton limestone, and the Canadian Corniferous limestone, although below  $150^{\circ}$ , in the limestone oils the proportions of the hydrocarbons  $C_nH_{2n+2}$  are relatively smaller and the aromatic hydrocarbons  $C_nH_{2n-6}$  relatively larger. These statements are made on the basis of results recently published (Mabery, *Proc. Amer. Acad.*, xxxii, 131). Study of the higher portions of Pennsylvania petroleum above  $220^{\circ}$  is now in progress for the purpose of separating without decomposition by distillation in vacuo, with consequent diminution of boiling points and exclusion of air, the constituents between  $216^{\circ}$  and  $400^{\circ}$ . This work has progressed sufficiently to show that the aromatic hydrocarbons of the series  $C_nH_{2n-6}$ , form only a comparatively small proportion of the distillates at least within the lower limits of temperature. It should be borne in mind that nothing is known concerning the principal or the subordinate constituents of American petroleum above  $250^{\circ}$ , except the possible presence of certain aromatic hydrocarbons, and these were recognized in products of ordinary distillation in which there is in-

variably much decomposition. To illustrate the effect of air at high temperatures on distillates with high boiling points, in a course of distillations in vacuo of Russian crude oil, accidentally air was allowed to enter a still in which distillation was proceeding without decomposition under a tension of 50 mm. at 250°. As soon as the air came into contact with the hot vapors, there was a violent explosion sufficient to send the thermometer out of the still and shatter it against a brick wall several feet distant. Air let into a still under similar conditions in which Pennsylvania oil is distilling usually causes flashes of light, but no explosion. From these observations it is evident that the advantage of distillation in vacuum depends as much at least on exclusion of air as on the reduction in temperature.

Definite statements relating to the composition of petroleum from different American fields must, at present, be limited to the distillates below 216°. But so far as it is possible to draw conclusions from data collected there seems to be no possibility of distinction based on geological occurrence and composition. High percentages of sulphur constituents are usually associated with limestone formations as the source of occurrence of the crude oils. But study of the varieties of crude oil from widely different sources leaves no basis for this distinction. A petroleum from South America occurring in a system of shales and sandstones contained 0.70 per cent. of sulphur (Mabery and Kittelberger, *Proc. Amer. Acad.*, xxxii, 185). Another variety from Oregon having no connection with a limestone formation also gave a high percentage, 1.19 per cent of sulphur. A specimen of petroleum from Japan, now under examination in this laboratory, gave 0.5 per cent. of sulphur. The immense deposits of petroleum in Roumania occurring in shales and sandstones are mostly high sulphur oils. No distinction can therefore be based on sulphur contents and geological occurrence.

It seems doubtful whether a distinction can be based on specific gravity and geological occurrence. The Pennsylvania oils differ from most others in their low specific gravity, varying in the main between 0.80 and 0.82; such light oils as the amber variety from Berea grit sandstone is as low in specific gravity as 0.79 (Mabery and Dunn, *American Chemical Journal*, 1896, 11). The limestone oils are higher, those from the Trenton limestone giving 0.82 to 0.85, and those from the Canadian Corniferous limestone 0.85 to 0.88. But the Russian oil, the South American oil mentioned above, the Japanese oil, and the Roumanian oil all show a high

specific gravity. With reference to the proportion of sulphur contents and specific gravity, it seems that all the high sulphur oils have a high specific gravity.

There is some hope of arriving at a general system of classification on the basis of the series of hydrocarbons which constitutes the main body of the crude oils. While more must be known concerning the composition of the constituents with higher boiling points before such a distinction can be made with desirable precision, I have seen sufficient of the behavior of the higher constituents to believe that such a basis is reasonable. As types of such a classification I should select on the one hand Pennsylvania oil, and on the other, Russian oil from the Baku district. The difference in specific gravity of the crude oils is borne out by the difference in specific gravity of the corresponding distillates, and individual constituents with the same boiling points. The typical constituents of Pennsylvania oil, at least below  $216^{\circ}$ , are members of the series  $C_nH_{2n+2}$ , but the components of the Russian as defined by the researches of Markownikow are the naphthenes of the series  $C_nH_{2n}$ . With reference to the ethylene series  $C_nH_{2n}$ , which has seemed to be accepted by some as constituting the main body of American petroleum, so far as my observation has extended, those hydrocarbons are not contained in any petroleum, at least below  $216^{\circ}$ , in more than minute quantities. Results which I have yet to publish show that these bodies are contained only in small proportions in limestone oils.

A classification of petroleum from all known sources evidently demands as its basis conclusive evidence as to the series of hydrocarbons of which each is chiefly composed. The methods to be pursued in reaching this knowledge have been indicated in my examination of Pennsylvania, Ohio and Canadian oils between  $150$  and  $216$  (*Proc. Amer. Acad.*, xxxii, 121). That the series  $C_nH_{2n+2}$ , constitutes the chief body of Pennsylvania crude oil below  $150^{\circ}$  was well established long ago by independent investigations. Above this point the evidence was less satisfactory. To accept the results of Pelouze and Cahours which continued the series  $C_nH_{2n+2}$  through the entire range of distillates to paraffine, it is necessary to ignore the fact that American petroleum is not composed exclusively of a single homologous series of hydrocarbons, but of a mixture of bodies that require for their separation, not only very prolonged fractional distillation, but searching and vigorous means of purification.



At the time when the French chemists conducted their investigations on American petroleum, both Pennsylvania and Canadian products were to be obtained in the European markets, especially in France, where Canadian oil seems to have been more easily obtained at times than Pennsylvania oil. In the papers of Pelouze and Cahours, allusions are made to American petroleum, and to Canadian petroleum. Their second paper (*Compt. Rend.*, 56, 505, 1863), begins with the following paragraph: "Dans un premier examen que nous avons fait des produits les plus volatils de l'huile provenant des forages qu'on pratique depuis quelques années sur plusieurs points de l'Amerique, et notement au Canada, nous avons signalé l'existenér d'un homologue du gaz des marais dont la composition est représentée par le formule  $C_{12}H_{14} = 4$  vol. vap."

With no previous knowledge as to the properties of crude oils from these different sources it would not be surprising if they were used indiscriminately. At any rate an examination of the papers of Pelouze and Cahours does not reveal the source from which their crude oil was obtained. But a comparison of their results as to specific gravity and percentage composition, together with their method of purification, with the same properties of distillates more thoroughly purified (Mabery, *loc. cit.*, p. 171), presents conclusive evidence that Pelouze and Cahours had in hand, in at least a portion of their work, distillates from Canadian oil. Furthermore, in some of their distillates showing a higher specific gravity than it is possible to obtain after suitable purification, even from Canadian petroleum, analytical values correspond closely to the series  $C_nH_{2n+2}$ ;  $C_{12}H_{26}$  at  $196^\circ$ - $200^\circ$ , and  $C_{13}H_{28}$  at  $216^\circ$ - $218^\circ$ . That Canadian crude oil was to be obtained in England at that time is evident from the work of Schorlemmer, who demonstrated the presence in oil from Canada of the aromatic hydrocarbons  $C_nH_{2n-6}$ .

The series  $C_nH_{2n}$ , found by Warren in Pennsylvania petroleum, has been accepted by some as showing the presence of the ethylene hydrocarbons, and by others as indicating the naphthenes. That the naphthenes are excluded below  $216^\circ$  in Pennsylvania oil by the wide difference in specific gravity has been pointed out (Mabery, *loc. cit.*, 125). The ethylene hydrocarbons are also excluded by the want of additive power in these distillates for the halogens.

Indeed, after removal of the aromatic hydrocarbons  $C_nH_{2n-6}$ , the series  $C_nH_{2n}$  disappears altogether from distillates within these

limits, leaving the series  $C_nH_{2n+2}$ , as representing the main body of Pennsylvania petroleum within these limits. The individual representatives of this series, when properly collected by fractional distillation and purification, include a decane at  $163^\circ-164^\circ$ , normal decane at  $173^\circ-174^\circ$ , undecane at  $195^\circ-196^\circ$ , and undecane at  $214^\circ-216^\circ$ . From Canadian petroleum a hydrocarbon collects at  $196^\circ-197^\circ$  whose percentage composition and molecular weight, as well as the composition of the monochlor-derivative, corresponds to the formula  $C_{11}H_{22}$ , and another at  $214^\circ-216^\circ$ , with the formula  $C_{12}H_{24}$ . The composition of all these hydrocarbons was ascertained by analysis, molecular weight determinations, analysis of chlorine derivatives, and molecular weights of the chlorine derivatives.

The impression that the higher portions of Pennsylvania oil are composed of naphthenes was perhaps not wholly without a reasonable foundation. After finding hexahydroisoxylol in Russian oil Beilstein and Kurbatoff identified the same body in Pennsylvania oil. Since no further attempts were then made to ascertain the composition of the higher portions, it was natural to infer that the results of Warren leading to the series  $C_nH_{2n}$  should be best explained by assuming that his bodies were naphthenes. After the discovery of the naphthene series in Russian oil by Markownikoff, this belief was strengthened by the erroneous assertions of Hoefer and other authors of German publications on petroleum that Markownikoff had established the naphthene series in Pennsylvania oil. A critical comparison of the specific gravity of Warren's hydrocarbons with those of Markownikoff without further work would have suggested doubts as to the presence of naphthenes in Pennsylvania oil at least below  $216^\circ$ .

It has long been an open question with oil men as to whether Ohio and Canadian petroleum is identical with Pennsylvania oil as regards the principal constituents. With respect to the portions distilling between  $150^\circ$  and  $216^\circ$ , this question has now been answered. The observed differences in the properties of distillates within these limits before purification concern, as has been shown, specific gravity and percentage composition. Before purification, however carefully the distillates have been separated by fractional distillation, analytical values correspond fairly well with the series  $C_nH_{2n}$ . After removal of the aromatic hydrocarbons the specific gravity is much reduced, and in the Pennsylvania distillates it corresponds to the specific gravity of the same hydrocarbons synthet-

ically prepared. Similar changes are produced in composition, the series changing to  $C_nH_{2n+2}$ . The series of aromatic hydrocarbons is represented in all the oils under consideration by numerous hydrocarbons, beginning with mesitylene at  $163^\circ$ . The higher homologues include cumol, pseudocumol, durol, isodurool, cymol, isocymol, and doubtless other higher members. Larger proportions of these bodies appear in Ohio than in Pennsylvania petroleum and still larger proportions in Canadian crude oil. After the most thorough purification with nitric acid and fuming sulphuric acid the distillates from Ohio and Canadian petroleum have a slightly higher specific gravity than the corresponding bodies from Pennsylvania oil, and the hydrocarbons from Pennsylvania oil show a specific gravity slightly higher than that of the hydrocarbons synthetically prepared. Schorlemmer thought that these differences in specific gravity were due to slight differences in isomerism, but it is quite possible that these oils contain very small percentages of naphthenes, especially if those bodies are slowly attacked by reagents, as Markownikoff observed in products from Russian oil.

If Pennsylvania petroleum, as typical of this class of crude oils, is composed within the limits between  $150^\circ$  and  $216^\circ$  of the series  $C_nH_{2n+2}$ , the individual hydrocarbons should resemble those prepared by synthetic methods. Unfortunately the structure of the synthetic hydrocarbons has not been determined in all instances with desirable precision, although they have been obtained from different sources. Normal decane boiling at  $173^\circ$  has a specific gravity 0.7456 at  $0^\circ$ , somewhat lower than the decane I have separated from petroleum. The boiling point of the latter body is  $173^\circ.5$ , and the specific gravity at  $20^\circ$ , 0.7486. The decane found in petroleum boiling at  $163^\circ$  may be diisoamyl since its specific gravity after the removal of mesitylene is not very different from that of diisoamyl. Its boiling point is somewhat higher than the boiling point of diisoamyl assigned by Wurtz. Hendecane from petroleum agrees fairly well in its properties with normal hendecane prepared by Krafft from rautenol. The boiling point of petroleum dodecane is the same as that of normal dodecane from laurinic acid, although the specific gravity of the petroleum hydrocarbon is somewhat higher than the other.

Since nothing has been done toward defining the butanes in petroleum except the rather superficial examination of the most volatile distillates in the early days of the petroleum industry, these



portions of the crude oil evidently invited further examination. The most volatile distillates of Pelouze and Cahours gave with chlorine a chlorbutyl boiling at  $65^{\circ}$ – $70^{\circ}$ , but nothing further was done toward identifying the hydrocarbon. Ronalds (*London Chem. Soc.*, 1865, p. 64) recognized a butane at  $0^{\circ}$ , but its form was not determined. Warren collected a distillate at  $0^{\circ}$ , and another at  $8^{\circ}$ – $9^{\circ}$ , which he inferred from analogy was a butane, but no further examination was made of these distillates. In our examination, after very prolonged distillation, using freezing mixtures for condensation, no distillate remained between  $5^{\circ}$  and  $20^{\circ}$ , thus excluding a butane at  $8^{\circ}$ – $9^{\circ}$ . At  $0^{\circ}$ , a large quantity of a hydrocarbon was obtained which gave a chlorbutane boiling at  $67^{\circ}$ – $68^{\circ}$ , the boiling point of isobutyl chloride. By decomposition of the chloride with alcoholic potassic acetate, an acetate was formed, and from the acetate an alcohol was obtained boiling at  $107^{\circ}$ – $108^{\circ}$ , which gave the percentages of carbon and hydrogen required for isobutyl alcohol. These facts, with the formation of isobutyl sulphide by treating the chloride with alcohol potassic sulphide, indicate that the hydrocarbon collected at  $0^{\circ}$  was isobutane, but they do not accord with the properties of butane and isobutane, the former of which, prepared by Frankland from ethyl iodide, boils at  $0^{\circ}$ , and the latter, prepared by Butlerow from tertiary butyl alcohol, boils at  $-17^{\circ}$ . Petroleum butane was prepared several different times from the most volatile refinery distillates we could procure, and always with the same results (Mabery and Hudson, *Proc. Amer. Acad.*, xxxii, 101). In reviewing the octanes in petroleum, we found one boiling at  $119^{\circ}.5$ , confirming the statements of Warren, and another boiling at  $124^{\circ}$ – $125^{\circ}$ , but no distillate remained above  $125^{\circ}$ . From the results of my work recently published, and what I have now in progress, it can, I think, be stated with confidence that it is useless to attempt to separate the constituents of petroleum boiling above  $220^{\circ}$  by the ordinary process of distillation, and whatever results have been published concerning distillates obtained in this manner shed no light on the constituents of the crude oils. Of course this is cold sympathy for those who desire to know more of these higher portions, since there is only one method, fractional distillation, for such separations, and this method can only be applied without decomposition by excluding air and reducing the boiling points. To illustrate its tediousness, early in October, two assistants started a distillation of 125 liters of Pennsylvania crude

oil applying a vacuum of above  $150^{\circ}$ . At present eight distillations have been made within  $2^{\circ}$  limits, up to  $300^{\circ}$  under 50 mm. Many repetitions within single degree fractions will be necessary to bring together the individual constituents.

The question is frequently asked whether paraffine is a normal constituent of the crude oil or is it a product of cracking. The answer is easy; paraffine is not obtained by cracking the crude oil, but it can itself be destroyed by cracking. If paraffine be contained in the crude oil it may be separated by distillation, provided cracking be not carried far enough to destroy it entirely. The presence of paraffine seems to be closely connected with the distinction mentioned between the series  $C_nH_{2n}$  and the series  $C_nH_{2n+2}$ . Higher distillates in vacuo of crude oils containing the series  $C_nH_{2n+2}$ , so far as I have observed, invariably deposit paraffine. Those oils consisting below  $216^{\circ}$  of the series  $C_nH_{2n}$  deposit no paraffine even when the highest distillates that can be collected are cooled to  $-20^{\circ}$ . It may be interesting to apply this distinction to those oils that have been carefully studied. With reference to the appearance of paraffine in distillates, it should be mentioned that it is observed only in the absence of serious cracking, and that it is easy in vacuum distillation to recognize the point where cracking begins. In distilling 125 liters of Pennsylvania crude oil mentioned above for the purpose of separating the higher constituents, approximately forty liters of residue above  $275^{\circ}$  under 50 mm. became nearly solid from the amount of paraffine deposited. With the hope that more distillate could be obtained without decomposition, the semi-solid mass was put back into the still and again distilled under 50 mm. Approximately two liters were collected in three distillates, none of which deposited paraffine, and the residue, on cooling, had the consistency of a thick tar, with no indication of paraffine. Paraffine separates from the higher distillates of Berea grit petroleum, as well as from all specimens of Ohio and Canadian oils that I have examined; but none separated from South American petroleum, from Oregon petroleum, nor from Russian Baku oil.

Since I began the study of petroleum, twelve years ago, I have devoted, considerable time to it, especially during the last seven years. Yet my results barely indicate the enormous field that awaits investigation in the examination of American petroleum. There is no field in industrial chemistry that offers greater inducements for fruitful results, both of scientific interest and practical

advantage, than the study of the portions of petroleum with high boiling points. There are immeasurably greater inducements for the establishment of a petroleum laboratory for research on American petroleums than have led to the opening of similar laboratories abroad. Such a laboratory, established solely for research, with funds equivalent to twenty thousand dollars a year, and employing a corps of ten competent research chemists, in five years would add greatly to the honor of American research, and would establish the composition of American petroleum. The lines of work that I have in sight, and have started experimentally, would be sufficient to occupy the attention of such a body of workers at least during two years. I should be glad to resign a considerable portion of this work to such a laboratory, or to any other competent investigators.

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#### DISCUSSION.

DR. SADTLER: I would like to say that there are one or two items referred to in Dr. Day's paper that may require a word. A paper appeared six months ago in a German journal by a gentleman named Heusler, in which he reported upon the action of aluminum chloride on the unsaturated series and perhaps on the aromatic series of hydrocarbons; and he claimed that by the heating of such mixtures with aluminum chloride (of course anhydrous aluminum chloride is meant), followed by distillation, carefully excluding moisture, he could readily and completely clear it by resinifying the unsaturated hydrocarbons and the aromatic hydrocarbons; any sulphur compounds could also be resinified; and he could then get by rectification absolutely pure hydrocarbons of the paraffin series.

That seemed to be a remarkable statement and one exciting attention; and a second article by the same author followed in the next number of the journal, in which he theorized a great deal upon Engler's menhaden oil products, and acknowledged having received from Engler by personal gift some portions of the distillates which he had obtained from these distillations of menhaden oil. He claimed that Engler's oils, when submitted to his treatment with aluminum chloride, had been purified and finally given the saturated hydrocarbons in rather small amounts. He then proceeded to theorize in what might hardly be called careful German style, but

rather a free and unguarded kind of way, having a theory of his own supplementing that of Engler, his theory being that Engler's distillates in their original conditions were more like the bituminous shale oils than true petroleum ; and that it needed this after-treatment with the aluminum chloride to bring them at all in character to correspond to petroleum oil. He therefore believed—assuming Engler's theory of the animal origin of oils—that these animal remains had first of all been subjected to a distillation analogous to that with bituminous shales ; and that a supplemental reaction with heat and contact with certain metallic chlorides—like the aluminum chloride, had transferred them into a secondary product, that is, the mixed petroleum or rock oil. The thing looked like a very fine solution of the question, but I have also noticed within the last six weeks two other articles published in the same journal, in which other authorities have claimed that this aluminum chloride reaction is a fallacy : that it does not by any means give a pure mixture of hydrocarbons belonging to the paraffin series and is absolutely worthless as a means of purification. It is stated that it cannot be carried out in the hands of any one except the gentleman who first published it. Prof. Day alludes to the possibility of sodium chloride playing an important part in the matter of producing these hydrocarbons of the Pennsylvania type from sulphur and oils similar to the Ohio type of oil. I doubt very much whether it is worth while to bring that in ; because the thing seems to be discredited and that part, of course, will have to drop away.

There is something to be said in favor of the question of filtration that Mr. McGonigle speaks of. As to whether the sulphur could be eliminated by that or any sodium chloride reaction I doubt extremely ; and therefore the theory which is presented by Dr. Day has several quite important breaks in it.

I need hardly make any comment upon the very interesting papers we have heard, first of Prof. Peckham and afterwards of Prof. Mabery. I have been acquainted for some time with Prof. Peckham's views with regard to liquid asphaltum and the way in which the change from petroleum may take place ; and there is an immense field, doubtless, there, to be opened and studied ; and then of course the whole thing is modified and very much complicated by the existence of what he calls hydrates of certain of these organic acids which are present ; and then the presence of these pyridine bases also has some modifying effect.

With regard to the very full statement which we have had from Prof. Mabery, I need only say that he has accomplished an immense amount of work; and nobody except those who undertake fractional distillation will understand anything of the enormous difficulty that he has had in this work and the amount of labor he has put upon it; the results which he has already attained and published are, in my opinion, far beyond the combined work of the several investigators who have previously published results on Pennsylvania oil and American petroleum without specifying its origin, as in the case of the two or three European investigators.

MR. JOSEPH WHARTON: I should like to ask whether any gentleman here can throw any light as to the physical condition of natural gas at the low depth at which it is found; whether it exists as gas at the depth of 2000 to 3000 feet, or whether it is condensed into a liquid form at that depth. Is there any one here who has knowledge upon that point?

PROF. MABERY: It seems probable that the gas should be liquefied under the great pressure to which it is subjected. That the pressure is enormous we know. It depends somewhat, doubtless, upon the structure that exists in those lower strata. Some very interesting experiments have been made in studying those strata, and I think it is probable from what is known that natural gas has existed in the liquid form.

MR. WHARTON: Does any one know what the critical point of natural gas is?

PROF. MABERY: I should say it would depend largely on the critical point of marsh gas. Liquefaction of this gas takes place under 180 atmospheres at  $11^{\circ}$  degrees Centigrade.

MR. WHARTON: Has there been any experiment as to artificial liquefaction of natural gas?

PROF. MABERY: Yes; all those gases have been liquefied.

PROF. PECKHAM: The sulphur in petroleum may be derived from two different sources: where there is a very small percentage, a fraction of one per cent., it may be that the sulphur was a constituent of the original material from which the petroleum was produced; but where the sulphur content has arisen to several per cent., as is often the case in the more dense liquid and solid bitumens, I think the sulphur has been produced by a reaction between the material of the bitumen itself, and salts—sulphates—in natural waters. It seems hardly possible that from any source—any animal or vegeta-



ble source—that as much as seven per cent. of sulphur could become a constituent of a bitumen; and I have found that amount in natural bitumen.

PROF. MABERY: I am much interested in the results Prof. Sadtler has presented. Although Engler should receive much credit for obtaining petroleum products by the distillation of menhaden oil under pressure, it should be remembered that Warren and Storer demonstrated many years ago that a lime soap formed from menhaden oil gives by distillation the petroleum hydrocarbons. Now Prof. Sadtler has shown that the same products may be obtained by distillation of vegetable oils under atmospheric pressure. This overthrows the favorite theory of the German authorities based on Engler's results, that petroleum was formed exclusively from animal remains. The formation of petroleum hydrocarbons from vegetable oils is extremely interesting, and we should congratulate ourselves that it has been done so near the early home of the petroleum industry.

In the work of Prof. Peckham, I am especially interested just now, because I have been trying for several years to procure specimens of California oil, to ascertain whether it is composed of the series  $C_nH_{2n}$  or the series  $C_nH_{2n+2}$ . I was recently informed that ten gallons of this oil is on its way to my laboratory. I examined an oil from Oregon which I was told resembles the California oil, and from comparison with small samples of the California products in my possession, that seems to be the case. The Oregon oil, and another from South America, contain the series  $C_nH_{2n}$ , but none of the series  $C_nH_{2n+2}$ . Pennsylvania, Ohio and Canadian petroleum give paraffine in abundance. Oils containing the series  $C_nH_{2n}$  seem to give no paraffine, so far as I have examined them.

Prof. Peckham has a great field for investigation in the California oil, both on account of the large amount of nitrogen compounds, and the question as to what series of hydrocarbons constitutes the main body of the crude oil.

PROF. PECKHAM: In reference to this matter of paraffine in petroleum, there have been two classes of petroleum discovered in California; one produced in the neighborhood of San José, the other in the Santa Clara Valley of the South. The great bulk of California petroleum comes from that southern valley; and so far as I know no traces of paraffine have ever been obtained from any of

it in any form—either what are known as the liquid nor the solid paraffines—not a particle of it has ever been obtained from any of the petroleum of the southern regions, but from that from the neighborhood of San José, scale paraffine has been obtained.

PROF. MABERY: Shale oil does not separate much paraffine; even in distillates above  $35^{\circ}$ .

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